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RECOMMENDED SPECIFICATIONS FOR LEADED ZINC OXIDE, DRY AND PASTE

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, JANUARY 12, 1920, P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; H. E. SMITH, U. S. RAILROAD ADMINISTRATION, SECRETARY.

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Railroad Administration, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specification to a large number of representatives of the paint and varnish industries, including the manufacturers of leaded zinc oxide, and gave careful consideration to the replies received in time].

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1. GENERAL

Leaded zinc oxide, frequently known as "Leaded zinc," consists of zinc oxide and varying amounts of lead compounds. It may be ordered in the form of dry pigment or paste ground in linseed oil. Purchases shall be made on the basis of net weight.

The pigment may be high-leaded zinc oxide or low-leaded zinc oxide. The contract shall state which kind is desired. The color and color strength when specified shall be equal to samples mutually agreed upon by buyer and seller.

The pigment shall meet the following requirements:

	Maximum	Minimum
	Per cent	Per cent
Coarse particles retained on Standard No. 200 screen ^a	0.0	

^a The No. 200 screen is the same as the screen formerly known as 100-mesh.

	High-leaded		Low-leaded	
	Maximum	Minimum	Maximum	Minimum
	Per cent	Per cent	Per cent	Per cent
Zinc oxide (ZnO).....		60		93
Water soluble salts	1.0		1.0	
Total impurities, including moisture.....	1.5		1.5	

The balance to be normal or basic lead sulphate.

The paste shall be made by thoroughly grinding the above pigment with pure raw or refined linseed oil. The paste shall not cake in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment.....	88.0	
Linseed oil.....		12.0
Moisture and other volatile matter.....	0.5	
Coarse particles and "skins" (total residue left on No. 200 screen based on pigment)	0.5	

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole.

With the dry pigment, the package is to be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4 (a). After assuring himself that the paste is not caked in the container, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with

a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

Samples will, in general, be tested by the following methods, but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specification.

3. LABORATORY EXAMINATION, DRY PIGMENT

(a) COLOR.—Take 5 g of the sample, add 1.5 cc of linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 5 g of the standard leaded zinc oxide. Spread the two pastes side by side on a clear colorless glass plate and compare the colors. If the sample is as white or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(b) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 0.2 cc of linseed oil, and rub up with a flat-bottomed glass pestle or muller; then add exactly 10 g of the sample and 2.5 cc of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner, except that 10 g of standard leaded zinc oxide is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(c) COARSE PARTICLES.—Dry in an oven at 105 to 110° C a standard No. 200 brass or copper sieve, cool, and weigh accurately. Weigh 50 g of pigment which has been previously thoroughly dried by heating in an oven at 105 to 110° C until all moisture is driven off. Transfer to a wide-mouth bottle or cylinder of about 300 cc capacity, add about 200 cc of dry kerosene, stopper, and shake vigorously for about five minutes. Remove stopper and wash back into the cylinder with a jet of kerosene any pigment adhering to the stopper. Pour about 50 cc of the kerosene with suspended pigment onto the sieve, let drain through, and

gradually transfer the whole of the kerosene and pigment to the sieve, finally using a jet of kerosene to transfer the last of the pigment. With proper manipulation a large portion of the pigment will pass through the sieve during the process of transferring from the cylinder. When all pigment has been thrown on the sieve, wash with a jet of kerosene until no more pigment passes through. To make sure that all particles have been thoroughly washed through, move the sieve from over the vessel in which the main portion of kerosene and pigment have been caught to over a clear glass dish resting on a black surface, and wash all portions of the sieve with a jet of kerosene, using not less than 200 cc of kerosene. This kerosene caught in this dish should be entirely free from pigment. If any pigment can be seen in the liquid, repeat washing until at least 200 cc can be washed through without showing any pigment. Then wash with a jet of kerosene all pigment adhering to the frame of the sieve beneath the wire mesh. Finally, wash the kerosene from sieve with petroleum ether, dry the sieve at 105 to 110° C, cool, and weigh. The increase in weight should be not more than 0.01 g.

(d) **QUALITATIVE ANALYSIS.**—Test for matter insoluble in hydrochloric acid, lead, calcium, carbon dioxide, etc., by regular methods of qualitative analysis.

(e) **MOISTURE.**—Place 1 g of the sample in a wide-mouth short weighing tube provided with a glass stopper. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

(f) **WATER SOLUBLE SALTS.**—To 10 g of pigment in a 500 cc volumetric flask, add 200 cc of water, boil for five minutes, nearly fill the flask with hot water, allow to cool, fill to mark, mix, filter through a dry paper, discard the first 50 cc of filtrate, transfer 100 cc of the filtrate (corresponding to 2 g of sample) to a weighed dish, evaporate to dryness, heat for one hour in an oven at 105 to 110° C, cool, and weigh, calculate to percentage of water soluble salts.

(g) **ZINC OXIDE.**—Weigh accurately about 0.3 g of the pigment, transfer to a 400 cc beaker, add 30 cc of hydrochloric acid (1 : 2), boil for two or three minutes, add 200 cc of water and a small piece of litmus paper; add ammonium hydroxide until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc of strong hydrochloric acid, heat nearly to boiling, and titrate with standard potassium ferrocyanide as in standardizing thae solution. (See Reagents 5 (d).) Calculate total zinc as ZnO.

(h) CALCULATIONS.—If, as will be the case with material complying with the specification, no metals but zinc and lead are found by qualitative tests, add the percentage of ZnO, moisture, and water soluble salts and subtract the sum from 100. Call the remainder “normal and basic lead sulphate.”

4. LABORATORY EXAMINATION, PASTE

(a) CAKING IN CONTAINER.—When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of leaded-zinc oxide paste. The paste shall be finally thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, 35 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle, the resulting mixture must be smooth and of good brushing consistency.

(c) MOISTURE AND OTHER VOLATILE MATTER.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(d) PERCENTAGE OF PIGMENT.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc “extraction mixture” (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C for two hours. Cool, weigh, and calculate percentage of pigment.

(e) EXAMINATION OF PIGMENT.—Grind the pigment from (d) to a fine powder, pass through a No. 80 sieve to remove any

"skins," preserve in a stoppered tube, and apply tests 3 (*d*), (*f*), (*g*), and (*h*). If required, apply tests 3 (*a*) and (*b*) in comparison with a portion of pigment extracted from the standard paste in exactly the same manner as in extracting the sample.

(*f*) PREPARATION OF FATTY ACIDS.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see Reagents) and 75 cc of ethyl alcohol; mix, and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice); boil, stir, and transfer to a separatory funnel, to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask, add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary, through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through CaCl₂ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C on a dry hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*g*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for five minutes, add 40 cc of water and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(h) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (f) in a small weighing burette or beaker;. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) COARSE PARTICLES AND "SKINS."—Weigh an amount of paste containing 50 g of pigment (see 4(d)), add 100 g of kerosene and wash through a No. 200 screen. The residue is reported as "coarse particles and 'skins,'" and should weigh less than 0.25 g.

5. REAGENTS

(a) URANYL INDICATOR FOR ZINC TITRATION.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(b) STANDARD POTASSIUM FERROCYANIDE.—Dissolve 22 g of the pure salt in water and dilute to 1000 cc. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc beaker. Dissolve in 10 cc of hydrochloric acid and 20 cc of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid and then add 3 cc of strong hydrochloric acid. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run using the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be

made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

(c) **BARIUM CHLORIDE SOLUTION.**—Dissolve 100 g of pure crystallized barium chloride in water and dilute to 1000 cc.

(d) **STANDARD SODIUM THIOSULPHATE SOLUTION.**—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g of crystallized sodium thiosulphate to 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine (See Analytical Chemistry, Treadwell-Hall, 2, 3d ed., p. 646). This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(e) **STARCH SOLUTION.**—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(f) **EXTRACTION MIXTURE.**—

10 volumes ether (ethyl ether).

6 volumes benzol.

4 volumes methyl alcohol.

1 volume acetone.

(g) **AQUEOUS SODIUM HYDROXIDE.**—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(h) **POTASSIUM IODIDE SOLUTION.**—Dissolve 150 g of potassium iodide free from iodate, in distilled water and dilute to 1000 cc.

(i) **HANUS SOLUTION.**—Dissolve 13.2 g of iodine in 1000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(j) **ALCOHOLIC SODIUM HYDROXIDE SOLUTION.**—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

WASHINGTON, January 12, 1920.

